Prediction of the Krichevskii parameter for volatile nonelectrolytes in water

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Abstract

The Krichevskii parameter, A_{Kr}, for aqueous solutes can be determined from variations of the vapor-liquid distribution constants for a solute at temperatures that are 100-150 K below the critical temperature of water. Pragmatically this means that if one can reliably evaluate the vapor-liquid distribution constant for a solute in water at temperatures up to 500-550 K, then the value of A_{Kr} for this solute can be calculated. This is exactly the approach taken in this study. We use a virial equation of state truncated at the second virial coefficient to evaluate the fugacity coefficients of the solute in the vapor phase and a simple empirical method of thermodynamic integration to calculate Henry's constant of the solute in water up to 550 K. These results allow prediction of the vapor-liquid distribution constants and the Krichevskii parameter for many volatile nonelectrolytes in water. It appears that the accuracy of predictions is limited mainly by the accuracy of the values of the thermodynamic functions of hydration of solutes at 298 K. The values of A_{Kr} for aqueous organic solutes follow group additivity systematics, and we derive a set of corresponding group contribution values for a large number of functional groups.

1. Introduction

The thermodynamics of infinitely dilute solutions near the solvent's critical point (for useful reviews see [1]-[3]) are governed by the value of the following derivative, which Levelt Sengers [2] has called the Krichevskii parameter, A_{Kr}:

$$A_{Kr} = \left(\frac{\partial P}{\partial x}\right)^{c}_{T,V,x=0}, \qquad (1)$$

with P and V being the pressure and volume of a system; T is the absolute temperature; x is the mole fraction of a solute; the superscript c indicates that the evaluation is done at the critical point of the pure solvent. The Krichevskii parameter appears in most applications of near-critical theory and governs such seemingly different problems as the initial coordinates of the critical lines, the sign and magnitude of the partial molar properties of a solute, etc. In other words, the Krichevskii parameter is the fundamental thermodynamic property of a solute at parameters corresponding to the critical temperature and the critical density/pressure of the solvent.

The goal of this work is to evaluate the values of the Krichevskii parameter for many volatile nonelectrolytes in water. Most methods of calculating A_{Kr} require accurate experimental data in the neighborhood of the critical point of the pure solvent: for example, initial slopes of the critical line or dew-bubble curves in a binary mixture, values of the partial molar volumes at near-critical conditions, etc. (see [2]-[5]) and, therefore, these "near-critical" methods are not particularly suitable for development of simple predictive schemes. However, as derived by Japas and Levelt Sengers [6], values of the Krichevskii parameter can also be determined from variations of the vapor-liquid distribution constants for a solute, K_D, according to the relation:

$$RT \ln K_D = 2A_{Kr}\frac{\rho - \rho_c}{\rho_c^2}, \qquad (2)$$

where $K_D = \lim_{x_2 \to o} \frac{y_2}{x_2}$, y_2 and x_2 are the vapor and liquid mole fractions of the solute; ρ and ρ_c are the liquid-phase density at saturation and the critical density of the solvent, respectively; R is the gas constant. Eq. (2) is the asymptotic relationship that must be valid in the neighborhood of the critical point of the pure solvent [6]. However, an analysis of K_D data for aqueous systems by the US and Argentine groups of researchers [6-8, 3] showed that the slope dictated by the Krichevskii parameter is nearly constant over 100-150 K below the critical point of water. This finding is empirical, but it is supported by the large variety of experimental results we have today, exemplified by a few experimental data [9-12] shown in Fig. 1. As a matter of fact, trust in the validity of Eq. (2) far away from the critical point of water is so compelling that Eq. (2) was used by Fernandez-Prini et al. [13] as a criterion of the internal consistency of high-temperature vapor-liquid equilibrium data.

Pragmatically this finding means that if one knows or can reliably evaluate the vapor-liquid distribution constant for a solute at temperatures up to 500-550 K, then the value of the Krichevskii parameter for this solute can be easily calculated. This is exactly the approach taken in this study. First, we use a virial equation of state truncated at the second virial coefficient to evaluate the fugacity coefficients of the solute in the vapor phase, ϕ_2^o.

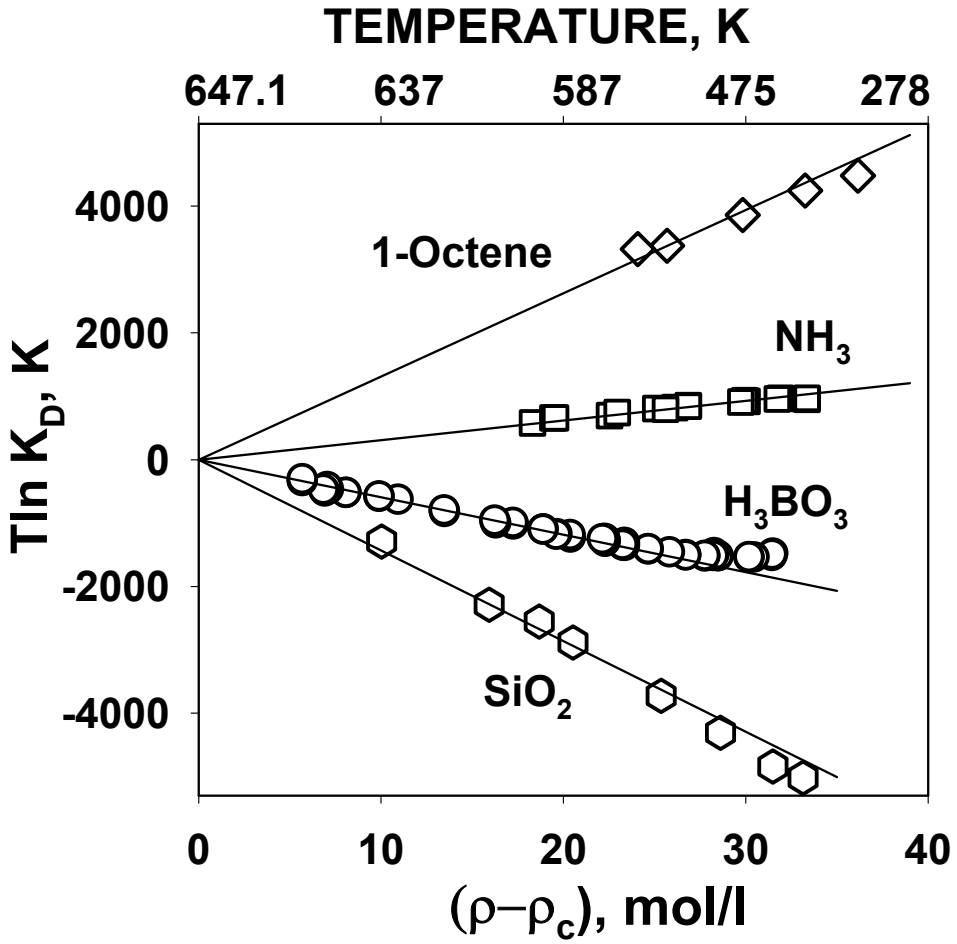

Fig.1. Examples of the relation given by Eq. (2). Vapor-liquid distribution constants for 1-octene, ammonia, boric acid and silica in water are taken from [9]-[12], respectively.

Second, we propose a simple empirical method of thermodynamic integration to calculate Henry's constant, k_H of the solute in water up to 550 K (Henry's constant is defined as $k_H = \lim_{x_2 \to o} \frac{f_2}{x_2}$, where f_2 and x_2 stand for the liquid-phase fugacity and mole fraction of the solute [8, 13]). These results allow prediction of the vapor-liquid distribution constants over the temperature range up to 550 K using the relation [8, 13]:

$$K_D = k_H / (\phi_2^o \cdot P_1^*), \qquad (3)$$

where P_1^* is the vapor pressure of pure water at saturation. Then Eq. (2) is employed to calculate the values of A_{Kr} for a solute in question.

2. Evaluation of ϕ_2^o for volatile nonelectrolytes in mixtures with water up to 550 K

At temperatures below 570 K the densities of steam are less than 50 kg·m^{-3}, and at such low densities only binary interactions contribute significantly to the deviations from

ideality of the thermodynamic properties of mixtures. Therefore, the virial equation of state truncated at the second virial coefficient will be adequate for representing the properties of the vapor phase, with the following relation for the fugacity coefficient of a solute at infinite dilution [14]:

$$\ln \phi_2^o = (2B_{12} - B_{11})\frac{P_1^*}{RT}, \quad (4)$$

where B_{11} is the second virial coefficient of pure water, which can be calculated from the IAPWS-95 formulation of the thermodynamic properties of water [15]; B_{12} is the cross (mixed) second virial coefficient for interactions between water and a solute. Elsewhere we present semiempirical methods for estimation of B_{12} [16], which were employed here for evaluating ϕ_2^o. Details are extensive and will not be repeated here. We just note that even relatively large errors in the predicted B_{12} values result in only moderate errors in the calculated $\ln \phi_2^o$ results, primarily because these errors are larger at lower temperatures where the saturated vapor pressure of water is low. For example, the errors in the B_{12} values of the magnitude of 500 and 30 $cm^3 \cdot mol^{-1}$ at 300 and 550 K will result in $\ln \phi_2^o$ errors of 0.002 and 0.08 units, respectively.

3. Evaluation of Henry's constants for volatile nonelectrolytes in water up to 550 K

Different methods can be used for evaluating Henry's constant at elevated temperatures, including approaches based on extensions of near-critical theories [17-18], etc. However, the simplest and most universal way of estimating k_H at temperatures up to 550 K appears to be the method of thermodynamic integration. This method exploits the connection between Henry's constant and the standard partial molar Gibbs energy of hydration (i.e. the Gibbs energy change associated with transfer of one mole of a compound from the state of the ideal gas at the reference pressure of 0.1 MPa to the state of the standard aqueous solution, defined as the state of unit activity in a hypothetical solution of unit molality referenced to infinite dilution at any temperature and pressure) given by the following relation:

$$\Delta_h G^o(T) = RT \ln \frac{k_H}{P^{\otimes}} - RT \ln \frac{1000}{M_w}, \quad (5)$$

where M_w=18.0153 $g \cdot mol^{-1}$ is the molar mass of water; $P^{\otimes}$ is the ideal gas standard pressure. The second term in the right hand side of Eq. (5) is needed for conversion between the molality concentration scale and the mole fraction concentration scale. Values of the Gibbs energy of hydration can be calculated by thermodynamic integration from a reference isotherm:

$$\Delta_h G^o(T) = \Delta_h G^o(T_r) - \Delta_h S^o(T_r)(T - T_r) + \int_{T_r}^{T} \Delta_h C_p^o(T) dT - T \int_{T_r}^{T} \frac{\Delta_h C_p^o(T)}{T} dT, \quad (6)$$

where $\Delta_h S^o(T_r)$ is the standard partial molar entropy of hydration at the reference point (values of $\Delta_h S^o$ are usually calculated from $\Delta_h G^o$ and the standard partial molar enthalpy of hydration, $\Delta_h H^o$, properties that can be measured directly, according to the relation $\Delta_h S^o = (\Delta_h H^o - \Delta_h G^o)/T$); $\Delta_h C_p^o(T)$ stands for the temperature-dependent heat capacity

of hydration. The natural selection for the reference isotherm is 298.15 K, where most experimental determinations of the thermodynamic functions of hydration are performed.

The values of the standard heat capacities of hydration at T>373 K are known only for a few nonelectrolytes. However, accurate calculations of the Gibbs energy of hydration at elevated temperatures do not require exceedingly accurate $\Delta_h C_p^o(T)$ values because of cancellation of errors in the $\Delta_h H^o(T)$ and $T \cdot \Delta_h S^o(T)$ terms, which both contribute to $\Delta_h G^o(T)$. This circumstance makes it feasible to look for a simple but general approximation for $\Delta_h C_p^o(T)$, the use of which will allow an accurate evaluation of $\Delta_h G^o(T)$ up to 550 K. Plyasunov and Shock [19] showed that the following relation will be sufficiently accurate for calculating $\Delta_h G^o(T)$ up to 550 K:

$$\Delta_h C_p^o(T) = a + b \cdot T, \qquad (7)$$

This approximation was verified by correlating $\Delta_h G^o(T)$ data for more than 30 aqueous nonelectrolytes, consisting of simple fluids (rare gases, methane, nitrogen, etc), nonpolar compounds (alkanes up to octane, cyclohexane, benzene, CO_2, ethane, etc), polar and hydrogen-bonded compounds (H_2S, ammonia, 1-propanamine, propanamide, alcohols, carboxylic acids). In other words, compounds with large differences in sizes and strengths of water-solute interactions were considered (for data sources and tables of results see [19]). It was found empirically [19] that the parameter b can be correlated with commonly available thermodynamic properties of hydration of a solute at 298 K:

$$b = 0.210 - 2.84 \cdot 10^{-3} \cdot \Delta_h C_p^o(298) - 8.04 \cdot 10^{-3} \cdot \Delta_h G^o(298), \qquad (8)$$

where units of $\Delta_h Cp^o(298)$ and $\Delta_h G^o(298)$ are $J \cdot K^{-1} \cdot mol^{-1}$ and $kJ \cdot mol^{-1}$, respectively. We expect that Eqs. (6)-(8) can be applied for reliable evaluation of $\Delta_h G^o$ and, therefore, Henry's constants for various volatile nonelectrolytes in water at temperatures up to 550 K. The errors in predicted values of k_H arise from the approximate character of the relation given by Eqs. (7)-(8), as well as uncertainties in the values of $\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ at the reference isotherm, 298 K. It is expected that in most cases the error in the predicted ln k_H values will be less than 0.25 units at 550 K [19].

4. Examples of evaluation of vapor-liquid distribution constants for volatile nonelectrolytes in water up to 550 K

Having in hand (essentially empirical) methods for prediction of ϕ_2^o and k_H for aqueous volatile nonelectrolytes in water up to 550 K, one should be able to calculate reliable values of the vapor-liquid distribution constants, K_D, for these solutes over the same temperature range, see Eq. (3). A few examples of such calculations are shown in Fig. 2. Up to 550 K our predictions describe the available data closely and confirm the success of the procedure proposed for evaluating K_D over the temperature range 273-550 K.

5. Evaluation of the Krichevskii parameter

Predicted K_D values at temperatures between 500 and 550 K were used for calculating A_{Kr} of the solute by means of Eq. (2). We expect that for compounds for which accurate

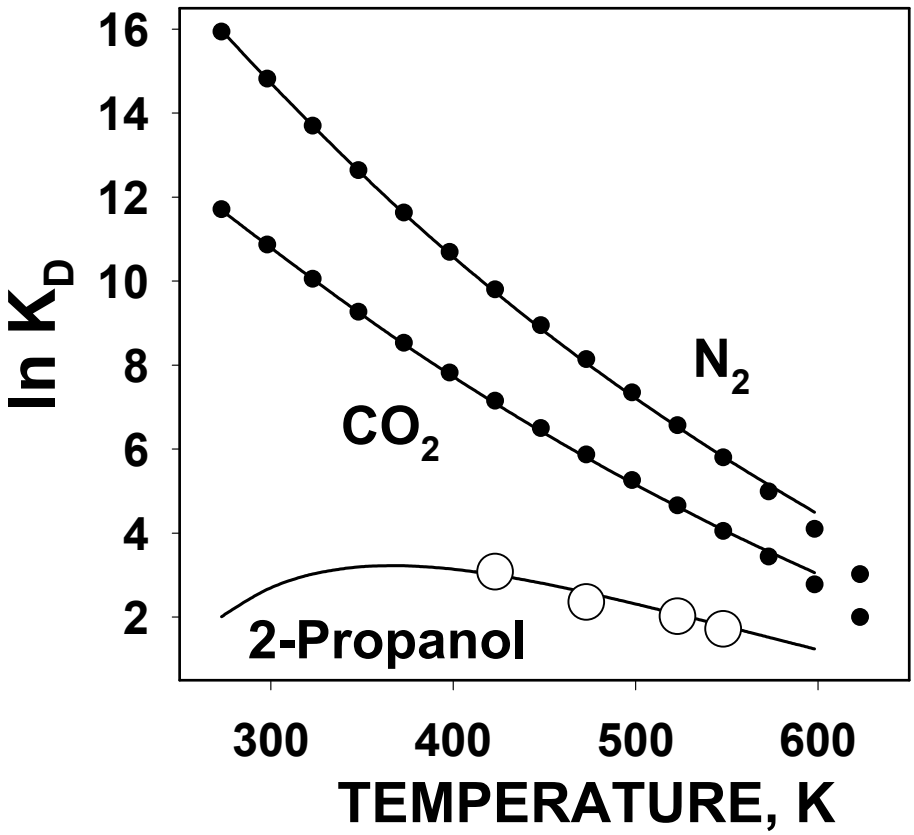

Fig.2. Experimental (symbols) and predicted (lines) values of ln K_D for some aqueous nonelectrolytes. Open circles represent data from [20], filled circles show values recommended in [13].

$\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ data are available at 298 K the predicted values of the Krichevskii parameter have uncertainties of ±7 MPa. It appears that the accuracy of predictions is limited mainly by the accuracy of the values of the thermodynamic functions of hydration of solutes at 298 K. In Table 1 we compare predicted and available A_{Kr} results for a few aqueous solutes. The most reliable values of the Krichevskii parameters are available for a few gaseous solutes considered in [13], and these results are given in bold in Table 1. Other values are quoted from compilation [5]. A more detailed comparison is available in [19]. In our opinion, data in Table 1 strongly suggest that the method proposed allows evaluation of the Krichevskii parameter for many aqueous solutes with accuracy close to the best determinations currently available. Calculated values of A_{Kr} for some inorganic compounds and halogenated derivatives of methane and ethene are present in Table 2. Values of the thermodynamic functions of hydration of solutes at 298.15 K necessary for calculations, and values of B_{12} are given and discussed elsewhere [19].

One can show that calculated values of A_{Kr} for organic compounds follow group additivity systematics, see Fig. 3. Therefore, we adopted a group additivity approximation

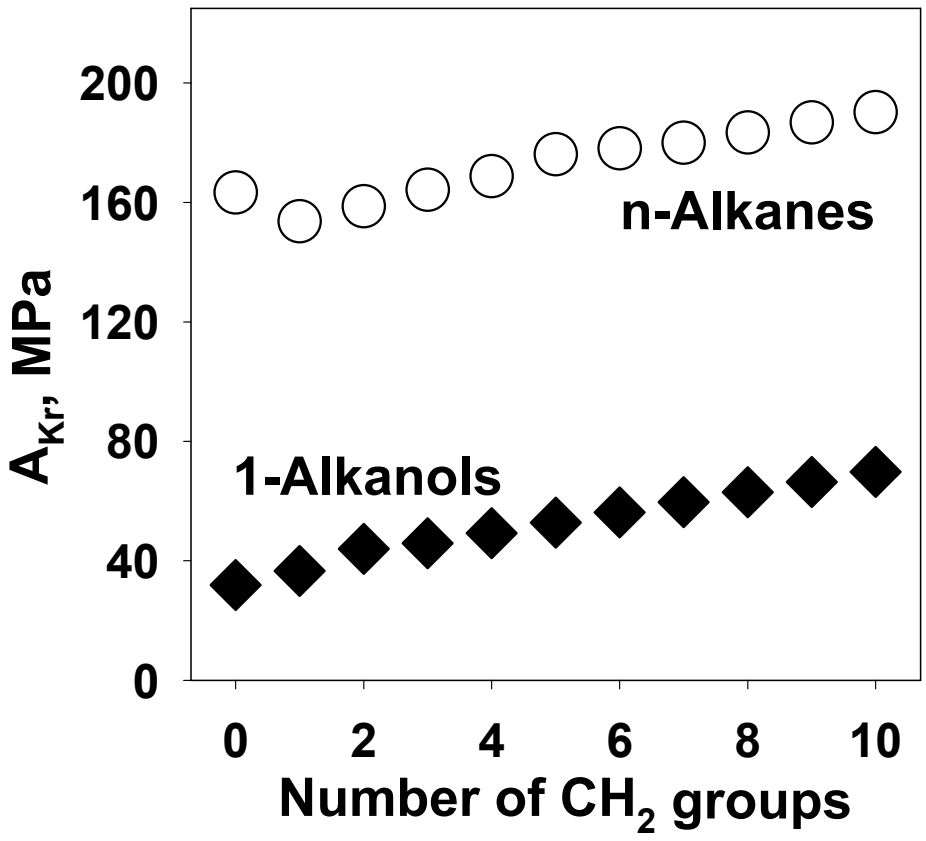

Fig.3. Predicted values of A_{Kr} for members of homologous series of normal alkanes and 1-alkanols. Compounds with zero number of CH_2 groups are ethane and methanol, respectively.

as an economic way to represent the A_{Kr} values for aqueous organic solutes. As done in previous studies [21-22, etc.], the property of an individual compound is considered as the sum of the properties of its functional groups plus the property of a nonintreacting point mass (or material point). The point mass can be considered as an example of a compound without groups at all, but with well defined values of the thermodynamic functions. It can be shown [19] that the value of the Krichevskii parameter for a point mass, $A_{Kr}(pm)$, is given by $A_{Kr}(pm)=RT_c/V_{1,c}$, where T_c and $V_{1,c}$ are the critical temperature and volume of the pure solvent. In the particular case of water, $A_{Kr}(pm)=96.17$ MPa. Therefore, the group contribution approximation for the Krichevskii parameter should be given as

$$A_{Kr} = A_{Kr}(pm) + \sum_i p_i A_{Kr,i} = \frac{RT_c}{V_{1,c}} + \sum_i p_i A_{Kr,i} , \qquad (9)$$

where p_i stands for the number of a functional group i in the structure of a compound, and $A_{Kr,i}$ represents the contribution of the group i to the value of the Krichevskii parameter. The values of $A_{Kr,i}$ for some functional groups in water are given in Table 4, and they are

expected to be useful for estimating the Krichevskii parameter for monofunctional compounds. Additional details of calculations are given in [19].

6. Conclusion

A simple and essentially empirical technique is proposed for calculating the vapor-liquid distribution constants, K_D, for volatile nonelectrolytes in water up to 550 K for volatile nonelectrolytes, for which the values of $\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ are known at 298 K. The values of the Krichevskii parameter, A_{Kr}, then can be readily calculated from values of K_D at 500-550 K. In this way we evaluated A_{Kr} for some inorganic and organic compounds in water. The values of A_{Kr} for organic solutes follow group additivity systematics, and we derive a set of corresponding group contributions to the Krichevskii parameter for a large number of functional groups.

Acknowledgements

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Table 1. Calculated and "experimental" values of the Krichevskii parameter for some aqueous nonelectrolytes from [13] (in bold) and [5].

Compound	A_{Kr}, MPa		Compound	A_{Kr}, MPa	
	Calculated	Literature		Calculated	Literature
Helium	168.6	**168.4**	Ammonia	43.5	40; 52
Neon	173.7	**186.3**	Tetrafluoromethane	202.5	210
Argon	163.0	**171.7**	Methane	162.6	**164.6**
Krypton	156.0	**169.2**	Ethane	162.8	**159.3**
Xenon	149.2	**150.3**	Propane	167.7	160; 153
Hydrogen	161.7	**169.9**	Hexane	165.7	151;197;170
Nitrogen	171.7	**177.5**	Cyclohexane	156.0	152; 130
Oxygen	166.0	**171.2**	Benzene	97.3	66; 95
Carbon monoxide	162.2	**174.3**	Toluene	104.7	105
Sulfur hexafluoride	212.9	**214.5**	Ethanol	37.5	52
Carbon dioxide	121.7	**124.3**	Piperidine	53.3	57
Hydrogen sulfide	96.6	**98.0**	Cyclohexanamine	56.2	57

Table 2. Calculated values of the Krichevskii parameter in water for some inorganic compounds and halogenated derivatives of methane and ethene.

Compound	A_{Kr} (MPa)	Compound	A_{Kr} (MPa)	Compound	A_{Kr} (MPa)	Compound	A_{Kr} (MPa)
Rn	126	H_2Se	115	CH_3Cl	103	CF_2Cl_2	170
NF_3	163	SO_2	69	CH_3Br	107	C_2H_4	141
D_2	156	HF	-15	CH_2FCl	101	1,2-$C_2H_2Cl_2$	72
CD_4	166	H_2O_2	-28	CHF_3	133	C_2F_4	150
PH_3	147	N_2H_4	-29	CHF_2Cl	125	C_2Cl_4	135
AsH_3	146	CH_3F	109	CF_3Cl	192		

Table 3. Calculated values of the Krichevskii parameter in water for some functional groups of organic compounds.

Group	A_{Kr} (MPa)	Group	A_{Kr} (MPa)	Group	A_{Kr} (MPa)	Group	A_{Kr} (MPa)
CH_3	29.33	C=C	-105.2	NH	-84.8	COH	-76.0
CH_2	3.55	HC≡C	-34.3	NH_2	-62.9	CO	-101.6
CH	-14.90	C≡C	-71.2	O	-38.9	CN	-111.0
C	-40.49	HC_{ar}	0.10	HS	-40.8	NO_2	-100.4
$C(CH_3)_2$	18.77	C_{ar}	-21.1	S	-67.8	$CONH_2$	-146.2
$C(CH_3)_3$	48.44	C_{fus}	-7.3	COO	-93.9	CONH	-198.8
H_2C=CH	7.8	C_{ar}–C_{ar}	9.7	F	-17.7	CON	-204.0
HC=CH	-29.7	CF_3	47.0	Cl	-12.8	COOH	-140.3
H_2C=C	-29.8	CCl_3	-35.9	Br	-19.3	OH	-90.1
HC=C	-67.3	N	-95.1	I	-12.9		